(12) UK Patent Application (19) GB (11) 2 222 179 (13) A

(43) Date of A publication 28.02.1990

(21) Application No 8822837.4

(22) Date of filing 29.09.1988

(30) Priority data
(31) 103862 (32) 01.10.1987 (33) US

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(51) INT CL[4]
C23C 4/02 14/02

(52) UK CL (Edition J)
C7F FARX FCD FGA FP811 FP820 FP841 FP852 FP853 FP861 FP862 FP864 FP887 FP901 FP902 FP914 FR914 F102 F103 F282 F441 F442 F809
U1S S1405 S1843 S1987

(56) Documents cited
None

(58) Field of search
UK CL (Edition J) C7B, C7F
INT CL[4] C23C

(54) **Protective coatings**

(57) Protective coatings such as ceramic coatings, which serve as thermal barriers, are applied to metallic substrates by first roughening the substrate surface to provide recesses in the surface which are jagged and which extend into the substrate at least about 600 microinches, the recesses being connected to the surface, and then disposing the protective coating in the recesses so that the coating is mechanically interlocked with the substrate at the recess. Preferably, the substrate surface is roughened by either electro-chemical machining or chemical etching. Convenient methods for applying a ceramic coating include plasma spraying, vapor deposition, and sputtering. In one embodiment, the substrate material is chosen from the group consisting of nickel-base, cobalt-base, and iron-base alloys, and the ceramic coating material is zirconia stabilized with another oxide.

The protected article finds use in aircraft engine applications.

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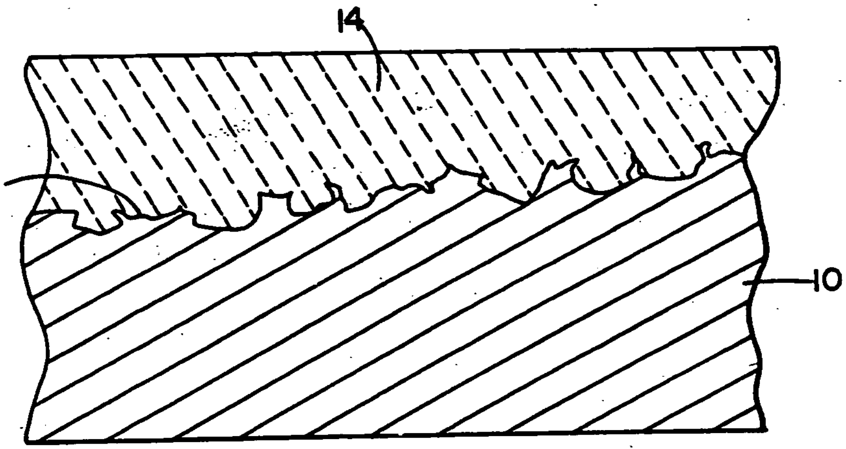

FIG. 1

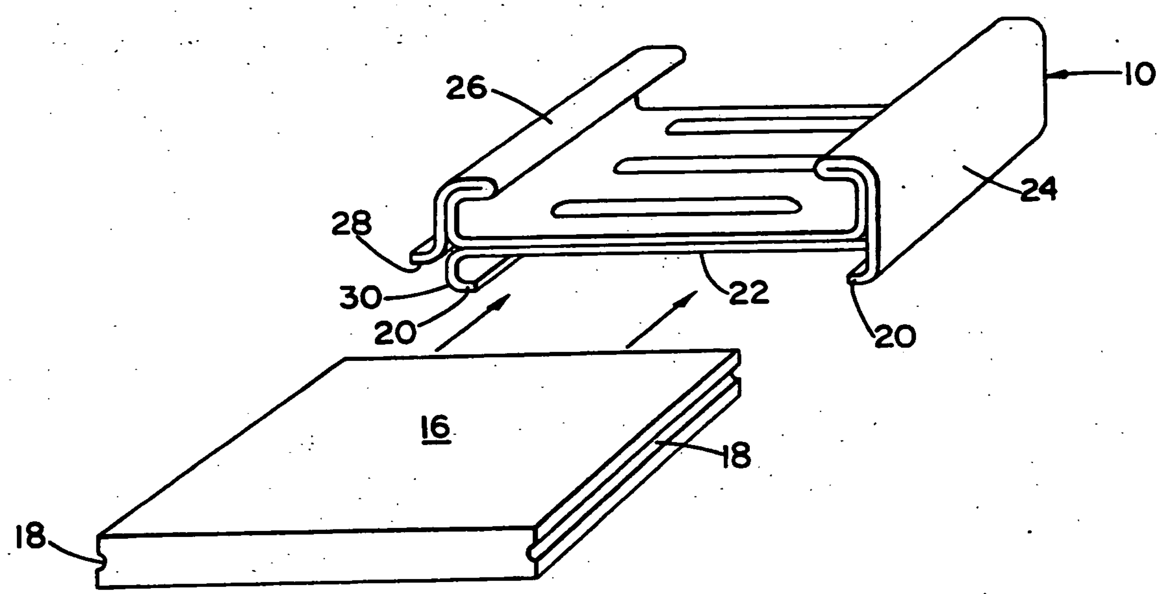

FIG. 2

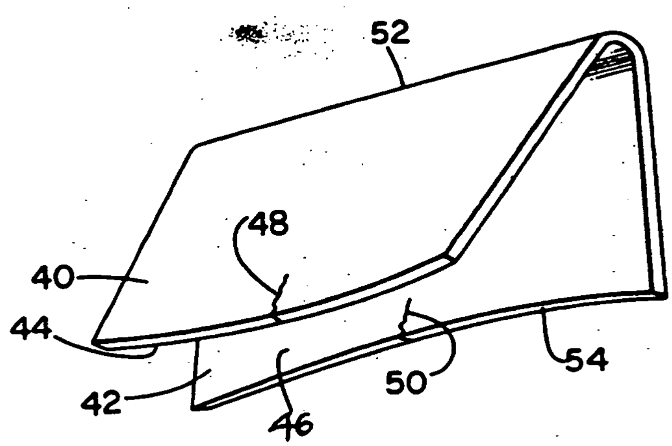

FIG. 3

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COATING SYSTEM

The Government has rights in this invention pursuant to Contract No. F33657-82-C-0195 awarded by the Department of Air Force.

Background of The Invention

This invention relates to protective coatings for metallic articles of manufacture which are exposed to high temperature environments. More particularly, it relates to ceramic coatings as in a thermal barrier coating system which does not require a bond coat between the ceramic layer and the metal substrate.

Combining the properties of ceramics with the properties of metals, especially superalloy metals, has been the subject of considerable scientific investigation. In one aspect of these investigations, attempts have been made to provide metal articles of manufacture with protective ceramic coatings, in order to combine the thermal properties of ceramics with the ductility and mechanical strength of metals. Ceramic coatings having low thermal conductivity act as thermal barriers which insulate and protect the underlying metal substrates from high temperatures and/or oxidizing conditions to which the substrates are exposed. Because of these properties, thermal barrier coatings are particularly useful for protecting the metal components of such apparatus as gas turbine engines and generators. In aircraft engine applications, the use of ceramic coatings on high pressure turbine shrouds and of thermal barrier coatings on other engine components is a key

aspect of the ongoing quest for higher turbine inlet temperatures, increased thrust-to-weight ratios, and improved specific fuel consumption. Application of such coatings to the superalloy metal components commonly employed in aircraft engine combustion chambers, transition ducts, after-burner liners, vane platforms, and airfoils in various stages, reduces both the temperature of the metal substrate and the effects of thermal transients thereon.

In the past, ceramic thermal barrier coatings have often been applied by plasma spraying techniques or by vapor deposition. To enable adhesion of the ceramic layer to the metal substrate, it has generally been required to employ a transition or superimposed bond coat which is a built-up layer between the metal and the ceramic. When applied to the metal substrate, the bond coat provides oxidation protection for the metal substrate and a relatively rough layer in which the ceramic particles are disposed to form a mechanical bond to the metal substrate. Amount the bond coat compositions commonly employed are the class of materials known as MCrAly alloys. Such alloys generally have a composition of from 5 to 40 percent chromium, 3 to 25 percent aluminum, 0.01 to 3 percent yttrium (or hafnium, lanthanum, cerium, or scandium), and a balance, M, selected from the group consisting of iron, cobalt, nickel and mixtures thereof. Thermal barrier coating systems utilizing these types of bond coats are well known in the art, and are described in such patents as, for example, US Patent No. 4,055,705 - Stecura et al. issued October 25, 1977, U.S. Patent No. 4,248,940 issued February 3, 1981 to G.W. Goward, et al., U.S. Patent No. 4,405,660 issued September 20, 1983 to N.E. Ulion, et al, and U.S. Patent No. 4,485,151 issued November 27, 1984 to S. Stecura, the disclosures of each of which are hereby incorporated herein by reference.

However, the use of a bond coat in the thermal barrier coating system limits the temperature to which the coated article of manufacture may be subjected. Many of the materials

used for a bond coat cannot withstand a temperature in excess of approximately 1,900°F, whereas the ceramic layer and the metal substrate can withstand temperatures considerably higher than that. Accordingly, in the use of such a coated article of manufacturer, the bond coat temperature limits maximum operating temperature of the thermal barrier coating system. Furthermore, such a superimposed bond coat adds weight to the finished articles of manufacture. Especially for such applications as in aircraft engines, the added weight attributable to the bond coat is a serious consideration. Inclusion of a bond coat in the thermal barrier coating system also requires extra processing steps, thereby increasing manufacturing costs and lengthening production schedules. Additionally, the bond coat is susceptible to degradation and failure which may, in turn, cause chipping, spalling, or cracking of the attached ceramic layer.

Accordingly, it is an object of the present invention to provide a thermal barrier coating system which does not require the above described type of transition or bond coat between the metal substrate and the ceramic thermal barrier coating.

It is also an object of the present invention to provide a thermal barrier coating system which is capable of withstanding higher temperatures than has heretofore been possible for thermal barrier systems employing such bond coats.

It is yet another object of the present invention to provide a method for applying thermal barrier ceramic coatings directly to metal substrates, without utilizing any transition or bond layers.

Summary of the Invention

In accordance with one aspect of the present invention, an article of manufacture having a protective coating such as a thermal barrier coating thereon comprises a metallic substrate having at least one roughened surface in which are provided

surface-connected, jagged recesses which extend into the substrate at least about 600 microinches, arithmetic average (AA). A ceramic thermal barrier coating is attached to the surface so that at least a portion of the coating is disposed into the recesses of the roughened surface of the substrate at the interface or bond line therebetween. In one embodiment, the substrate comprises a material selected from the group consisting of nickel-base, cobalt-base, and iron-base alloys, and the ceramic coating consists essentially of zirconia stabilized with another oxide.

In another aspect of the present invention, a method for coating a metal substrate with a protective coating such as a thermal barrier material comprises roughening at least one surface of the metal substrate so that the resulting surface exhibits a profilometer reading of at least about 600 microinches AA. Convenient and preferred surface roughening are selected from chemical etching, electrochemical etching and laser surface treatment. A protective coating such as a ceramic thermal barrier coating then is applied to the substrate so that at least a portion of the coating is disposed into the recesses of the roughened surface of the substrate. The coating may be applied to the roughened substrate surface by a variety of methods, for example, plasma spraying, vapor deposition, or sputtering. In order to achieve a stoichiometric ceramic composition, the thermal barrier coating may be heated in an oxygen-containing atmosphere.

Brief Description of the Drawings

The subject matter which is regarded as the invention is particularly pointed out and distinctly claimed in the concluding portion of the specification. The invention itself, however, both as to its organization and its method of practice, together with further objects and advantages thereof, may best be understood by reference to the following

description taken in conjunction with the accompanying drawing, in which:

Figure 1 is an enlarged, fragmentary, cross-sectional view diagrammatically illustrating a metallograph of a portion of a coated article of manufacture in accordance with one embodiment of the present invention;

Figure 2 is an exploded perspective view diagrammatically illustrating an article of manufacture to which a thermal barrier coating is to be applied, in accordance with another embodiment of the present invention; and

Figure 3 is a perspective view diagrammatically illustrating the appearance of a thermal-barrier-coated article of manufacture in accordance with the present invention, after being subjected to thermal cycle testing.

Detailed Description of the Preferred Embodiments

Figure 1 diagrammatically illustrates a cross section at about 32 magnifications of a portion of a metallic article having a durable ceramic thermal barrier coating thereon, in accordance with the present invention. Metallic substrate 10 has at least one roughened surface 12 to which ceramic thermal barrier coating 14 is attached. Coating 14 is disposed on substrate 10 so that at least a portion of coating 14 is situated directly in contact with roughened surface 12. In accordance with the present invention, roughened surface 12 exhibits a profilometer reading of at least about 600 microinches AA and is characterized by having jagged recesses as shown in Figure 1.

Substrate 10 may comprise a wide variety of structures. Generally, substrate 10 may be any metal structure which benefits from an adherent coating such as one providing a thermal barrier. In one particularly useful embodiment, substrate 10 is an article suitable for use in structures having high mechanical strength and high resistance to

temperature and corrosion. In such an embodiment, substrate 10 comprises a material selected from the group consisting of nickel-base, cobalt-base, and iron-base alloys. Included in this group of materials are the alloy compositions which have become known as superalloys, based upon their exceptional properties at elevated temperatures. For gas turbine engine applications, it is often desirable for the material chosen for substrate 10 to be strong as well as resistant to oxidation and corrosion at high temperatures. Typical alloy compositions possessing these characteristics include those listed in the following Table 1.

TABLE 1

SUPERALLOY COMPOSITIONS

Nominal Weight Percent Plus Incidental Impuritie

Alloy	Fe	Cr	Al	Ti	Y_2O_3	Ni	C	Co	Mo	W	Cb	Ta	Re	Hf	B	Zr	Y
MA956	Bal	20	4.5	0.5	0.5												
Ma754	1	20	0.3	0.5	0.6	Bal	0.05										
Rene' N4		9.3	3.7	4.2		Bal		7.5	1.5	6	0.5	4					
Rene' N5		7	6.2			Bal	0.05	7.5	1.5	5		6.5	3	.15	40ppm		100ppm
Rene' 80		14	3	5		Bal	0.17	9.5	4	4					.015	0.03	
MAR-M-509		22.5				10	0.6	Bal		7		3.5				0.5	

The material chosen for ceramic coating 14 should exhibit, among other properties, low thermal conductivity, adequate adherence to substrate 10 for resistance to thermal stress spalling and cracking, a thermal expansion rate which is matched as close as possible to that of substrate 10, and adequate stabilization of the ceramic crystal structure to minimize the effects of volume expansion caused by structural transformation.

Zirconium oxide often is employed in thermal barrier coating systems because it is an efficient thermal barrier. For superior stability, it has been found that the zirconia material should consist of mixtures of cubic and tetragonal phases. It has further been established that partial stabilization of the zirconia with another oxide, such as yttrium oxide, produces this desired mixture of phases. Preferably, ceramic coating 14 comprises zirconia partially stabilized with between about 6 percent and 20 percent by weight of yttria. Less than about 6 percent by weight of yttria does not produce the desired partial stabilization. On the other hand, more than about 20 percent by weight of yttria results in full stabilization of the zirconium oxide. In many thermal barrier coating applications, between about 6 percent and about 8 percent by weight of yttrium oxide is preferred.

During initial evaluations of the present invention it was recognized that the degree of surface roughness and the character of the roughness in combination are unexpectedly significant in the ability of a superimposed ceramic coating to mechanically bond securely to a roughened substrate. Known bond coats, such as of the thermally sprayed MCrAlY type, were noted to have a surface roughness in the range of about 450-550 microinch (AA). Superimposed ceramic coatings adhered to such a surface during long cycles of thermal testing. However, without such a bond or transition layer, surface roughness in such lower ranges resulted in inadequate bonding. For example, grit blasting of a surface generally results in a surface roughness in the range of about 100 - 250 microinch (AA).

In regard to the character of the surface, it was recognized that, in addition to a relatively high degree of roughness for example as measured by a profilometer, the surface must have a "jagged" configuration as represented by Figure 1, to enable good mechanical linking or bonding between the roughened surface and a superimposed ceramic coating. For example, a surface which was treated or roughened by electrodischarge machining (EDM) well known and widely reported and used in the art, had a surface roughness of about 750 microinch (AA). Yet tests showed that severe cracking developed along its bond line with a ceramic coating. It is believed that this resulted from the condition of the recast layer on the roughened surface.

By way of contrast, a surface roughened with electrochemical machining (ECM), also well known and widely reported and used in the art for material renewal but not adjusted for surface roughening, had a surface roughness in the range of 600 - 1000 microinches (AA) and showed no bond line cracking in the same test. According to the present invention, such results are attributed to the surface including jagged, tooth-like structures, as shown in Figure 1, as well as a surface roughness of at least about 600 microinches (AA).

Representative of the test results obtained in the

evaluation of the present invention are the data in the following Table 2.

TABLE 2

JETS Thermal Cyclic Tests - 2000 Cycles
(Top Ceramic: ZrO_2 - $8Y_2O_3$, 0.005" thick)

Example	Specimen	Surface Prep	Surface Roughness (microinch AA)	Results (d)
1	Standard (a)	Bond Coat	450 - 550	No bond line cracks
2	No bond coat (b)	ECM	600 - 950	No bond line cracks
3	No bond coat (b)	EDM	750	Severe bond line crackir
4	No bond coat (c)	Gritblasted	100 - 250	Severe bond line crackir

(a) CoNiCrAlY Bond Coat (0.005")/Rene' 80 alloy substrate
(b) Substrate: Roughened MA956 alloy (Brazed to Rene' 80 alloy backing)
(c) Substrate: Rene' 80 alloy
(d) Periodic 50 - power microscopic examination

In Table 2 as well as in the following Table 3, the thermal cyclic testing was conducted on a Jet Engine Thermal Shock (JETS) rig, designed, built and reported by the assignee of the present invention in MACH 3 Magazine, March/September 1987, published by G.E. Aircraft Engines, Production Operation, "Ceramic Tough New Breed of Shroud". The JETS rig basically consists of four

sections: (1) a heating/cooling assembly, (2) a test specimen support on a vertical carrousel, (3) an electronic indexing and stepping motor drive, and (4) temperature measuring and monitoring equipment. An oxygen-propane torch allows rapid heating (about 20 seconds) of the ceramic face on 1 inch diameter button specimens. The next station subjects the specimens to a rapid quench (approximately 20 seconds to below 500°F) between air jets which impinge on both the ceramic surface and metal backing. Temperatures on both such sides are measured with optical pyrometers.

In the evaluations represented by the data of Tables 2 and 3, the thermal barrier ceramic coating of ZrO_2 stabilized with 8 weight percent Y_2O_3 was air plasma sprayed to the thicknesses identified. Each cycle in Table 2 heated each specimen to the following condition: average ceramic surface temperature 2230°F (1221°C); average metal backside temperature 1595°F (868°C); average temperature difference 635°F (353°C). Thereafter, the specimen in each cycle was cooled to below about 500°F, as described above.

TABLE 3

JETS Thermal Cycle Tests - 2500 Cycles
(Top Ceramic: ZrO_2 - $8Y_2O_3$, avg. 0.036 - 0.038" thick)

Example	Specimen	Surface Prep	Surface Roughness (microinch AA)	Results (c)
5	Standard (a)	Bond coat	450 - 550	No bond line cracking
6	No-bond coat (b)	ECM	700 - 950	No bond line cracking

(a) CoNiCrAlY Bond Coat (0.005")/Rene' 80 alloy substrate
(b) Substrate: Roughened MA956 alloy (brazed to Rene'80 alloy backing)
(c) Periodic 50 - power microscopic examination

Each cycle in Table 3 heated each specimen to the following condition: average ceramic surface temperature 2567°F (1408°C); average metal backside temperature 1208° (653°); average temperature difference 1359°F (755°C). Thereafter, the specimen in each cycle was cooled to below about 500°F, as described above.

Comparison of the data in Table 2 and in Table 3 clearly shows the dramatic effect of the present invention on coating integrity: the combination of degree of surface roughness along with the character of such roughness can provide a significantly improved thermal barrier system for high temperature applications.

In a particular example employing Rene' N5 alloy as the substrate, a chemical etch was used to roughen the specimen surface. Such a roughening process is particularly attractive for such a material which is a single crystal alloy the nominal composition for which is shown in Table 1. The chemical etching resulted in a surface roughness in the range of about 600 - 800 microinches (AA) with a 2-4 mils depth of etch. In addition, such an etching technique can take advantage of the difference in chemical composition and etching characteristics between dendrites and the interdendritic region of such alloys as Rene' N5. Acid etching produced a rough surface (up to 800 microinches AA) uniquely adapted to receive and hold a ceramic coating overlayer. Additionally, tips of dendrites extending into the ceramic coating can have some effect on crack formation within the ceramic, thereby providing a strain relief mechanism near the interface. Adjustment of the parameters of the well known electrochemical machining process (ECM), generally used to removed substantial amounts of metal to shape an article surface, can accomplish similar results depending on the substrate article.

In the above chemical etch example involving Rene' N5 alloy, the etching bath was an aqueous solution predominantly

of HCl with a small amount of HNO_3 and including $FeCl_3$ at about 50 wt percent $FeCl_3$ to water. Etching was conducted for about 1 hour at about ambient temperature.

For applications where it is desireable, the coated article of manufacture of the present invention may further comprise one or more preformed structures of ceramic material, with each preformed structure being mechanically attached to at least one surface of the metal substrate, in the manner illustrated in Figure 2. The preformed ceramic structure may be made in a predetermined shape and thickness, which thickness may significantly exceed the thickness readily attainable for air plasma sprayed ceramic coatings. In the particular embodiment shown in Figure 2, the preformed structure comprises ceramic slab 16 having a pair of retaining grooves 18 formed along opposite edges of slab 16. Means for mechanically attaching slab 16 to surface 22 of substrate 10 comprises a pair of retaining tabs 20 associated with retaining grooves 18, with retaining tabs 20 disposed so that each tab 20 is in locking engagement with one of retaining grooves 18. Retaining tabs 20 are formed as an integral part of substrate 10 and are configured so as to retain ceramic slab 16 in position with respect to substrate 10. The remaining surfaces of substrate 10, such as surfaces 24, 26, 28, and 30, may comprise roughened surfaces to which a ceramic coating may be applied, in the manner illustrated in Figure 1 by surface 12 and coating 14. In such an embodiment, the ceramic thermal barrier coating may be made to completely encapsulate substrate 10 and may be comprised of sections having several different thicknesses.

The thermal barrier coating systems described hereinabove can be formed without utilizing any intermediate, built-up bond coat layer between the protective ceramic and the underlying structure. In accordance with the present invention, a method for coating a metal substrate with a thermal barrier material comprises roughening at least one surface of the metal substrate as described above and applying thereto a ceramic

thermal barrier coating. The ceramic coating is applied so that at least a portion thereof is situated within the jagged recesses in the roughened surface of the substrate. The roughening step is carried out so that the roughened substrate surface exhibits a profilometer reading of at least about 600 microinches AA. A more preferred range is between about 600 and 1,000 microinches AA.

The substrate surface may be roughened by a number of different techniques. According to the present invention it has been found that electro-chemical machining (ECM) and chemical etching are two particularly effective methods for producing a roughened substrate surface. As used in the material removal art, a goal of electro-chemical machining is to produce a smooth surface finish. For example, ECM is commonly employed in the manufacture of aircraft engine components to meet the smoothness requirements imposed by aerodynamic and mechanical design considerations. However, the present invention has found that, by varying such process parameters as amperage, ram travel, nozzle flow rate, and the electrolyte solution, electro-chemical machining can also be utilized to provide a roughened metal surface of the type suitable as a bonding surface for ceramic thermal barrier coatings. For example, electro-chemical machining has been employed to produce surface roughnesses exhibiting profilometer readings in the range of between 700 and 1,000 microinches AA, for metal alloy substrates having compositions of MA 956 and MA 754 alloy compositions listed in Table 1. The resulting roughened metal surfaces were characterized by distinct peaks and valleys, and had a rough, grainy texture similar to the textures exhibited by air plasma sprayed bond coats.

Similar roughened surfaces may be produced by a chemical etching process. By appropriately choosing the etchant solution and the time the substrate is immersed in the etchant, as described above in connection with Rene' N5 alloy, a variety of desired surface roughnesses may be achieved. For example,

surface roughnesses exhibiting profilometer readings of between about 600 and 900 microinches AA have been produced by chemically etching metal alloy substrates having compositions of the Rene' N4 and Rene' N5 alloys shown in Table 1.

For substrates which are formed by metal casting techniques, it may be desirable to provide the roughened substrate surface as part of the casting process. The roughening step of the present invention may be accomplished during formation of the metal substrate by casting the substrate in a mold which itself has a roughened surface, with the roughened surface of the mold being configured so as to impart a corresponding roughened surface to the as-cast substrate. For example, selected wax die mold surfaces may be roughened by knurling, etching, or electro-chemical machining techniques. Once the roughened mold surfaces have been achieved, normal investment casting processes may be used to form the substrate. The resulting as-cast substrate structure includes at least one surface portion having sufficient character and roughness, according to the present invention, to function as a bonding surface for a ceramic thermal barrier coating.

The ceramic thermal barrier coating may be applied to the roughened substrate surface by a number of methods. Suitable techniques include plasma spraying, vapor deposition, and sputtering. All of these techniques are well known in the art and widely reported. Generally, in plasma spraying, powder particles having the desired material composition are transported from a plasma gun to the target surface by a hot gas stream. The powder particles are heated to a molten state by the hot gas stream and resolidify upon being deposited on the target surface. In vapor deposition, the article to be coated is positioned over a molten pool of material having the desired composition. As the material evaporates, the resulting vapor condenses on and coats the article. The vapor deposition process is conveniently carried out in a vacuum chamber, and an

electron beam is often used as a heat source to keep the material heated to the molten state.

For thermal barrier coatings containing oxides, the as-deposited ceramic resulting from the above application techniques may be oxygen deficient. When such coatings are employed in the method of the present invention, the thermal barrier coating may be additionally processed by heating it in an oxygen-containing atmosphere so as to achieve a substantially stoichiometric ceramic composition. For partially stabilized zirconia oxide ceramics, heating the coating in air for about 4 hours at a temperature of about 1,975°F is generally sufficient. It should be noted that, in some applications, the coated article undergoes annealing during conditions of use, in which case the temperature annealing step described above is not necessary.

In some thermal barrier coating applications, the desired thickness of the ceramic coating may exceed the thickness readily attainable using the ceramic coating processing techniques described hereinabove. For such applications, the method of the present invention may further comprise mechanically attaching at least one preformed structure of ceramic material to at least one surface of the metal substrate as described above in connection with Figure 2.

Of course, as a preparatory step for any of the processing techniques included in the present invention, it may be desireable to thoroughly clean the surface which is to be roughened or coated. Dirt, grease, oxides and the like may be removed by any number of suitable cleaning methods known in the art.

In another evaluation of the present invention, a MA 956 alloy structure known in the aircraft engine art as a v-gutter was coated with a thermal barrier material in accordance with the present invention, and tested in a cyclic temperature flame tunnel burner rig. The inner surface of both trailing flaps of the v-gutter were roughened by electro-chemical machining, and

a 0.020 inch thick ceramic coating of zirconia stabilized with 8 percent by weight of yttria was applied to the roughened surfaces by air plasma spraying. The coated v-gutter structure was thermal cycle tested in a flame tunnel test rig which produces higher operating temperatures than the thermal shock test rig used in the above examples and which has a pressurized heating system. During the heating portion of the test cycle, a flame produced by autoignition of pressurized jet fuel heated the specimen, at a pressure of 100 pounds per square inch over atmospheric pressure (PSIA), to a temperature of approximately 2,300°F, over a period 22.5 seconds. During the cooling cycle, a water quench was used to cool the specimen, at a pressure of 85 PSIA, to a temperature of approximately 1,900°F, over the same period of 22.5 seconds.

The thermal-barrier-coated specimen successfully completed 1,000 of these burner rig test cycles. The thermal barrier coating system remained completely intact with no apparent ceramic spallation. The ECM-roughened surface again provided an excellent bonding surface for adherence of the ceramic to the metal substrate. The appearance of the v-gutter after 1,000 thermal cycles is illustrated in Figure 3. The ECM-roughened surfaces having the ceramic coating applied thereto are shown in Figure 3 as inner surfaces 44 and 46 of trailing edge flaps 40 and 42. During the testing, two small cracks, denoted in Figure 3 by reference numerals 48 and 50, developed in the trailing edges of the v-gutter structure. Each crack was approximately 0.300 inches in length and was located at approximately the mid-span area of the respective trailing edge flap. These cracks were probably due to the relatively large temperature gradient that existed across the flaps during temperature cycling. During testing, the v-gutter was firmly held in position by two v-gutter end caps. The end caps were positioned in the test rig, and the entire apparatus was ensconced in the water trough, in such a manner that the cooling water caused the end caps and, correspondingly, the top

and bottom portions of the v-gutter to be much cooler than the mid-span area of the flap. The resulting thermal gradient across each flap induced a maximum thermal stress at the mid-span thereof, and probably resulted in formation of cracks 48 and 50 shown in Figure 3. Furthermore, it should be noted that this v-gutter structure simulates the after-burner component of an aircraft engine and is considered to have failed only if the structure is completely severed into two separate pieces. Theoretically, as cracks 48 and 50 propagate towards leading edge nose radius 52 of the v-gutter, the thermal gradient and the resulting thermal stress across each flap will decrease to a level such that each crack ceases to propagate or grow any further.

The foregoing describes a thermal barrier coating system which does not require a bond coat build-up between the metal substrate and the ceramic thermal barrier coating. The present invention provides a thermally protected article of manufacture having a durable ceramic coating which is securely bonded to the substrate. By eliminating the need for such a bond coat, the present invention provides a finished article which is lighter in weight and which can withstand higher operating temperatures than has heretofore been possible using conventional thermal barrier coating systems. Furthermore, by providing a method for applying thermal barrier ceramic coatings directly to metal substrates, the present invention also reduces manufacturing costs and production schedules.

While the invention has been described in detail herein in accord with certain preferred embodiments thereof, many modifications and changes therein may be effected by those skilled in the art. For example, while the invention has been described with respect to several specific examples thereto, the ceramic and metal compositions, as well as the processing techniques, described therein are intended to be exemplary rather than limiting. Accordingly, it is intended by the appended claims to cover all such modifications and changes as fall within the true spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. An article of manufacture including a protective coating carried by an article metallic substrate, wherein:

the metallic substrate has a surface in which there are provided jagged recesses which extend into the substrate at least about 600 microinches (Arithmetic Average, AA) the recesses being connected to the surface.

2. The article of claim 1 in which the coating is a ceramic coating disposed into the recesses, providing a mechanical interlocking between the surface and the ceramic coating.

3. The article of claim 2 in which the ceramic coating is a thermal barrier coating based predominantly on zirconium oxide.

4. The article of claim 3 wherein:

the substrate is a superalloy based on at least one element selected from the group consisting of Ni, Co and Fe;

the recesses extend into the substrate in the range of about 600 - 1000 microinches (AA); and

the thermal barrier coating is predominantly zirconium oxide stabilized with another oxide.

5. The article of claim 4 wherein:

the substrate is a nickel base single crystal superalloy structure; and

the thermal barrier coating is predominantly zirconium oxide stabilized with about 6 - 20 weight percent yttrium oxide.

6. The article of claim 4 wherein the thermal barrier coating is applied to a thickness of at least about 0.005 inch.

7. The article of claim 6 in which the coating is applied to a thickness in the range of about 0.005 - 0.050 inch.

8. The article of claim 1 comprising:

the metallic substrate;

at least one preformed structure of a ceramic material; and

means for attaching said preformed structure to the article.

9. In a method for preparing an article metallic substrate for application of a protective coating, the step of:

providing the substrate with a surface having jagged recesses which extend into the substrate at least about 600 microinches (AA) so that the recesses are connected to the surface.

10. A method for applying a protective coating to a metallic substrate comprising the steps of:

roughening a surface of the substrate to provide in the surface recesses which are jagged and which extend into the substrate at least about 600 microinches (AA), the recesses being connected to the surface; and

disposing the protective coating in the recesses so that the coating is mechanically interlocked with the substrate at the recesses.

11. The method of claim 10 for applying the protective coating to the metallic substrate wherein:

the roughening is provided by a metal removal method selected from the group consisting of electrochemical removal, chemical etching and laser etching.

12. The method of claim 10 for applying the protective coating to a cast metallic substrate wherein:

the roughening is provided in the surface by precision casting the recesses into the substrate during casting of the substrate.

13. The method of claim 10 for applying a ceramic coating to a substrate of a superalloy based on at least one element selected from the group consisting of Ni, Co and Fe, comprising the steps of:

roughening a surface of the substrate to provide in the surface recesses which are jagged and which extend into the substrate in the range of 600-1000 microinches (AA); and

disposing the ceramic coating in the recesses so that the coating is mechanically interlocked with the substrate at the recesses.

14. The method of claim 13 for applying a ceramic thermal barrier coating to a nickel base superalloy substrate, in which:

the roughening is provided by a metal removal method selected from the group consisting of electrochemical removal, chemical etching and laser etching.

15. The method of claim 13 in which the ceramic coating is disposed by a coating application method selected from the group consisting of vapor deposition, plasma spray deposition and sputtering.

16. The method of claim 14 wherein:

the thermal barrier coating is predominantly zirconium oxide; and

the roughening is provided by electrochemical removal.

17. The method of claim 14 wherein:

the thermal barrier coating is predominantly zirconium oxide; and

the roughening is provided by chemical etching.

18. The method of claim 14 for applying a ceramic thermal barrier coating to a nickel base alloy single crystal substrate in which:

the roughening is provided by chemical etching; and

the ceramic thermal barrier coating is predominantly a stabilized zirconium oxide.

19. The method of claim 18 in which the thermal barrier coating is predominantly zirconium oxide stabilized with about 6 - 20 weight percent yttrium oxide.

Published 1990 at The Patent Office, State House, 66/71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office. Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD. Printed by Multiplex techniques ltd, St Mary Cray, Kent, Con. 1/87